

## Some extra info on introducing entropy changes

### The basic explanation

To get around the problem of many compounds dissolving freely in water despite the fact that their enthalpies of solution are endothermic you have to introduce the concept of **entropy change**.

The only way of making sense of entropy without getting bogged down in some serious maths is to think of it as a measure of the amount of disorder in a system. Entropy is given the symbol **S**. If a system becomes more disordered, then its entropy increases.

In order to see whether a change is possible or not, you have to think about a combination of the enthalpy change and the entropy change. These can be combined mathematically to give an important term known as **free energy change**.

The diagram shows the equation  $\Delta G = \Delta H - T\Delta S$  in blue. Red arrows point from labels to the terms: 'enthalpy change' points to  $\Delta H$ , 'entropy change' points to  $\Delta S$ , 'free energy change' points to  $\Delta G$ , and 'temperature (K)' points to  $T$ .

As an approximation, for a reaction to happen, the free energy change must be negative.

What happens if the enthalpy change is positive - as for example when sodium chloride dissolves in water (+3.9 kJ mol<sup>-1</sup>, using the values in one of the tables above)?

As long as the entropy change is positive enough, it is possible to get a negative value for free energy change. In the sodium chloride case, you don't have to have very much increase in entropy to outweigh the small enthalpy change of +3.9 kJ mol<sup>-1</sup>.

The diagram shows the equation  $\Delta G = \Delta H - T\Delta S$  in blue. A red arrow points from the text 'If entropy change is positive enough, the negative value of  $-T\Delta S$  will outweigh the positive value of  $\Delta H$ .' to the  $-T\Delta S$  term. Another red arrow points from the text 'ΔG will then become negative, and the change is feasible.' to the  $\Delta G$  term.

So . . . does the entropy increase when sodium chloride dissolve in water? Yes, it does!

Originally, the sodium and chloride ions were arranged in a very tidy way in the crystal lattice - their entropy was low. (Remember that entropy is a measure of *disorder*.) When you dissolve the crystal in water, the entropy increases as the ions and water molecules become completely jumbled up - they become much more disordered than they were originally.

This is where the explanation usually stops, but to stop at this point is very misleading because it won't explain all the facts!

### What's wrong with this explanation?

The most obvious thing that's wrong is that it won't explain why some compounds (like magnesium carbonate, and most of the other Group 2 carbonates) don't dissolve in water even though their enthalpies of solution are mainly negative.

In these cases, the entropy of the system must *fall* when the compounds dissolve in water - in other words, the solution in water is more ordered than the original crystal and water!

The diagram shows the equation  $\Delta G = \Delta H - T\Delta S$  in blue. A red arrow points from the text 'ΔG must be positive because the change isn't happening to any extent.' to the  $\Delta G$  term. Another red arrow points from the text 'If this is negative, the only way of making ΔG positive is for  $-T\Delta S$  to be positive.' to the  $-T\Delta S$  term. A third red arrow points from the text 'That only happens if ΔS is negative - if the system becomes more ordered than it was before.' to the  $\Delta S$  term.

This happens because the *water molecules* become more ordered when the compound dissolves in them. Instead of milling around pretty much at random, they become attracted to the ions present and arranged around them.

This is particularly effective if the ions are small and highly charged - and so the effect is greatest for the positive ions at the top of the Group, and gets less as you go down. It is also much more important in Group 2 than in Group 1 where the ions only carry one positive charge.

That means that you have two entropy effects to consider. There is the increase in *disorder* as the crystal lattice breaks up, but a corresponding increase in *order* in the water - which varies depending on the sizes and charges of the ions present.

What a nightmare!

To explain this properly, you need to think about the way lattice enthalpy changes as you go down the Group, the way that hydration enthalpies change, and the way that entropy changes. The way those changes happen will vary from one type of compound to another.

### Can we explain everything now?

No - at least not easily! For example, although it might be possible to account for the lack of pattern in the solubilities of the Group 1 chlorides (and also the bromides) by a mathematical application of these effects, trying to do it in general terms defeats me completely!

You could, however, make a reasonable suggestion as to why the solubility trend in the carbonates is broken at barium. (Don't expect the explanation to be instantly understandable though!)

Remember that the solubility of the carbonates falls as you go down Group 2, apart from an increase as you go from strontium to barium carbonate.

The general fall is because hydration enthalpies are falling faster than lattice enthalpies. Remember that where you have a big negative ion, its size dominates the inter-ionic distance and so doesn't allow the lattice enthalpy to change much. This gives the enthalpy of solution values we've already looked at (values in  $\text{kJ mol}^{-1}$ ):

$\text{MgCO}_3$	-25.3
$\text{CaCO}_3$	-12.3
$\text{SrCO}_3$	-3.4
$\text{BaCO}_3$	+4.2

But the entropy change will also be varying as you go down the Group. At the top, where you have small  $2+$  ions, the overall entropy change in the system must be negative - the system as a whole becomes more ordered when the compound dissolves because of the way the water molecules become organised around the positive ions. That negative entropy change is going to be enough to wipe out the effect of the exothermic enthalpy of solution.

Towards the bottom of the Group, this effect changes. The bigger ions have less organising effect on the water molecules. The entropy change is becoming less negative (or perhaps even at this stage, positive). That's going to tend to make the compounds more soluble.

The overall effect is a complex balance between the way the enthalpy of solution varies and the way the entropy change of solution alters. At barium carbonate, the effect of increasing entropy must be enough to make it more soluble than strontium carbonate.